

# Theoretical Comparison of Maser Materials for a 32-GHz Maser Amplifier

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*This report presents the computational results of a comparison of maser materials for a 32-GHz maser amplifier. The search for a better maser material is prompted by the relatively large amount of pump power required to sustain a population inversion in ruby at frequencies on the order of 30 GHz and above. The general requirements of a maser material and the specific problems with ruby are outlined. The spin Hamiltonian is used to calculate energy levels and transition probabilities for ruby and twelve other materials. A table is compiled of several attractive operating points for each of the materials analyzed. All the materials analyzed possess operating points that could be superior to ruby. To complete the evaluation of the materials, measurements of inversion ratio and pump power requirements must be made in the future.*

## I. Introduction

This report describes the results of a theoretical evaluation of several paramagnetic materials being considered for use in a 32-GHz maser amplifier. Previously, ruby has been very successfully employed in 2.3- and 8.4-GHz masers [1], and in an 18- to 26-GHz tunable maser [2]. However, due to a monotonically decreasing inversion ratio above 12 GHz for ruby (for push-pull pumping) ruby becomes less favorable at higher frequencies. The inversion ratio is defined as the ratio of the inverted-spin population difference with the pump on to the thermal-equilibrium population difference with the pump off, and is determined experimentally by the ratio of gain (dB) with the pump on, to absorption (dB) with the pump off. Moore and Neff [3] and Shell (private communication) measured an inversion ratio of 1.1 at 32 GHz. In a recently completed reflected-wave maser [5], the inversion ratio was estimated to be 0.7 to 0.8. This low inversion ratio was a contrib-

uting factor to the reduced gain-bandwidth of the maser compared to a similar 22-GHz maser [31] in which the inversion ratio was at least 1.6. Theoretical calculations of spin-lattice relaxation rates [29] suggest that the low inversion ratio ( $I \approx 1$ ) is inherent in ruby at this operating point ('operating point' refers to a given dc field strength, crystal orientation, and pumping scheme). Hence, other paramagnetic materials, as well as other operating points of ruby, are investigated as a first step toward finding the best maser material at 32 GHz.

Before proceeding with the materials evaluation, two points should be made. First, the inversion ratio in the 32-GHz reflected-wave maser (RWM) could probably be improved by either using more pump power or by using a maser structure with a higher Q at the pump frequency. In the former case, heating of the maser due to microwave losses will degrade the

gain and noise temperature performance, but to what extent is unknown. In the latter case, the resonant structure would significantly reduce the tunability of the RWM, but would improve the pump power coupling over a still useful instantaneous bandwidth. However, even with these engineering improvements, the inversion ratio would still only approach unity.

The second point is that the inversion ratio, even though central to the evaluation of a maser material, cannot be accurately addressed by the methods presented here. It is believed that the low inversion ratio of ruby at the 32-GHz RWM operating point is a result of an unfavorable set of spin-lattice relaxation rates. These relaxation rates and the corresponding inversion ratios have been calculated, but, due to the complexity of the calculations, will be presented in a future report.

In Section II the requirements of a maser material are discussed, including the difficulties with ruby. A list is provided of the materials evaluated. In Section III the use of the spin Hamiltonian to calculate energy levels and transition probabilities is outlined. In addition, limits on the inversion ratio and a material figure-of-merit are discussed and the method of computation is reviewed. In Section IV a table of several promising operating points is presented for each of the materials analyzed. The conclusions are presented in Section V. The Appendix contains a table of measured relaxation times obtained from the literature for several materials of interest.

## II. Maser Material Considerations

The choice of a maser material is the single most important factor in maser design. The maser material consists of a non-magnetic crystalline lattice lightly doped (0.01–0.1 percent) with paramagnetic ions. Detailed discussions of suitable paramagnetic ions and host crystals are given elsewhere [6], [7]. Here, only an outline of the necessary and desirable material properties is given.

The most common paramagnetic ions are transition metals and rare earths, because of their unfilled  $3d$  and  $4f$  electron shells. To operate in CW mode, the ion should possess an orbital ground state with three or more spin levels. This eliminates most of the rare earths. The additional requirement of a negligible nuclear magnetic moment (a source of inhomogenous broadening) reduces the possible ions to  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Gd}^{3+}$ . (Actually, it is not clear that such broadening would adversely affect a maser with an inhomogenous applied field.) Only Cr and Fe are considered here, as they are by far the most common choices of active ions. The electronic configurations of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  are  $3d^3$  and  $3d^5$ , respectively. The cor-

responding free-ion ground states are  ${}^4F_{3/2}$  and  ${}^6S_{3/2}$ . Hence,  $\text{Cr}^{3+}$  has four spin levels and  $\text{Fe}^{3+}$  has six.

The host crystal must be non-magnetic, non-metallic, and available in large single crystals of a high degree of perfection. The material should have a sufficiently high thermal conductivity and small loss tangent at liquid helium temperatures and microwave frequencies to minimize heating of the lattice. To facilitate the microwave engineering, the crystal should possess a relatively isotropic and temperature-independent dielectric constant. Finally, the material should be machinable and chemically stable, and be able to withstand thermal cycling between liquid helium and room temperatures.

The active ion substitutes for one of the metal ions in the crystal lattice. The local crystal electric field seen by the ion splits the highly degenerate orbital ground state into degenerate pairs (assuming the number of spin levels is even). This splitting of spin levels due to the crystalline electric field is termed the zero-field splitting (ZFS). The ZFS must be large enough to permit pump-induced transitions between non-adjacent spin levels. As a rule-of-thumb, the ZFS should be of the same order of magnitude as the signal frequency.

Another very important material parameter is the spin-lattice relaxation time, which describes how long spins remain in an excited state before returning to thermal equilibrium with the lattice. At microwave frequencies, spin-lattice interaction is the dominant spin relaxation mechanism. For relatively low concentrations of paramagnetic ions (<0.05 percent) and at liquid helium temperatures, the most significant spin-lattice interaction is thought to be the Kronig-Van Vleck mechanism [8], in which lattice vibrations induce transitions between spin states, and spin-spin interactions are neglected. The spin-lattice relaxation times of the various transitions must be long enough ( $\geq$  msec) to permit saturation of the pumped levels with a reasonable amount of pump power. Impurities, ion clustering, and dislocations (all of which are a function of the crystal growth procedure) can shorten relaxation times, so pure, defect-free crystals are preferable.

Another material parameter is the (unbroadened) linewidth  $\Delta f_L$  of the material. At liquid helium temperatures,  $\Delta f_L$  is determined primarily by spin-spin interactions and is inversely proportional to the spin-spin relaxation time, which is the average length of time between random dephasing “collisions” of neighboring spins [9]. The linewidth is usually within the range of 10–100 MHz for solid-state maser materials. For linear stagger-tuned masers of bandwidth  $\gg \Delta f_L$ ,  $\Delta f_L$  can be shown to have no first-order influence on the gain-bandwidth properties of the maser (see Section III). However, if the taper is along the length of the material, a material with a smaller  $\Delta f_L$  may exhibit a larger noise temperature at one end of its band-

pass [9]. At present, it is not understood how  $\Delta f_L$  impacts pump power requirements.

Finally, many materials possess two or more magnetically inequivalent sites (i.e., sites having different spectra) for the active ions to occupy, thus decreasing the density of useful ions. (Gain in dB is proportional to spin density.) In most materials, certain orientations exist for which these sites become equivalent. For such materials, only these orientations will be analyzed.

As mentioned in Section I, difficulties were experienced using ruby at 32 GHz. A relatively low inversion ratio was obtained for the orientation employed in the 32-GHz RWM. The pump transitions in ruby at this orientation are quite weak, making it difficult to saturate the levels. This is a result of the small zero-field splitting (ZFS) of ruby: ZFS = 11.4 GHz, which is only about one-third of the signal frequency. To obtain sufficient separation between spin levels for amplification at 32 GHz, a relatively large magnetic field (11.8 kG) must be applied. This field becomes the dominant influence on the spins, far exceeding the effects of the local crystal field. Under such conditions, the spins in the lattice assume nearly pure-spin characteristics, as if the Cr ions existed freely in the magnetic field. The selection rules of quantum mechanics allow transitions only between adjacent pure-spin states [10], thus leading to a small stimulated transition probability for the pump transitions in ruby. A material with a larger ZFS will in general have stronger pump transitions and will therefore better absorb the pump power, all other factors remaining the same.

The materials analyzed in this work are listed below. Details of the crystal structure, orientation of magnetic axes, spin Hamiltonian, and site equivalence are given in the references.

Ruby ( $\text{Al}_2\text{O}_3:\text{Cr}$ )	[11]
Emerald ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}$ )	[12]
Spinel:Cr ( $\text{MgAl}_2\text{O}_4:\text{Cr}$ )	[13]
YAG:Cr ( $\text{Y}_2\text{Al}_5\text{O}_{12}:\text{Cr}$ )	[14]
YGG:Cr ( $\text{Y}_2\text{Ga}_5\text{O}_{12}:\text{Cr}$ )	[14]
Rutile:Cr ( $\text{TiO}_2:\text{Cr}$ )	[15]
Zinc Tungstate:Cr ( $\text{ZnWO}_4:\text{Cr}$ )	[16]
Andalusite:Cr ( $\text{Al}_2\text{SiO}_5:\text{Cr}$ )	[17]
Yttrium Oxide:Cr ( $\text{Y}_2\text{O}_3:\text{Cr}$ )	[18]
Rutile:Fe ( $\text{TiO}_2:\text{Fe}$ )	[19]
Zinc Tungstate:Fe ( $\text{ZnWO}_4:\text{Fe}$ )	[20]

Andalusite:Fe ( $\text{Al}_2\text{SiO}_5:\text{Fe}$ ) [21]

Sapphire:Fe ( $\text{Al}_2\text{O}_3:\text{Fe}$ ) [22]

### III. Evaluation of the Spin Hamiltonian and Associated Parameters

The spin Hamiltonian  $H_s$  describes the interaction of the electron spin of the paramagnetic ion with the local crystal field and with the applied magnetic field. Evaluation of  $H_s$  allows calculation of the energy levels and transition probabilities for the spin system of a singlet orbital ground state ion in a radiation field. Detailed discussions of the spin Hamiltonians may be found in the literature [8], [23]. Berwin [24] gives a detailed derivation of the spin Hamiltonian based on the formulation of Bleaney and Stevens [23] for ruby. In [25], Berwin discusses the spin Hamiltonians for several of the materials listed in Section II.

For most materials of interest, the assumption of an “intermediate” crystal field is made, meaning that the interaction energy of the crystal field with the ion falls between the Coulomb and spin-orbit interaction terms. In deriving  $H_s$ , the spin-orbit and Zeeman terms are treated together as a perturbation on the singlet orbital ground state. The absence of orbital degeneracy is sufficient for quenching of the orbital angular momentum  $L$  [8]. That is, to first-order,  $L$  is equal to zero, so the ion behaves in a pure-spin-like manner. Up to a second-order perturbation, the spin-orbit coupling admixes the singlet ground state with higher-lying orbitals, restoring some of the orbital angular momentum. This second-order effect is the source of the ZFS.

For ruby, the spin Hamiltonian has the form [11]

$$H_s = g\beta\bar{B} \cdot \bar{S} + DS_z^2 \quad (1)$$

where the spectroscopic splitting-factor is  $g \approx 2$  ( $g = 2.0023$  for pure spin),  $\beta$  is the Bohr magneton,  $\bar{B}$  is the applied dc magnetic field, and

$$\bar{S} = \hat{x}S_x + \hat{y}S_y + \hat{z}S_z \quad (2)$$

is a vector of spin operators. The spin operators describe the observable properties of the paramagnetic ion spin states and may be conveniently written in matrix form [10]. The Cartesian directions are along the principal axes of the magnetic complexes. These axes, usually expressed in terms of the crystallographic axes, are used to describe the symmetry of the magnetic resonance spectrum. The orientation of  $\bar{B}$  is expressed by the usual azimuthal and polar angles,  $\phi$  and  $\theta$ . The constant  $D$  determines the ZFS and reflects, in principle, the

extent of admixing with higher lying orbitals. This spin Hamiltonian exhibits axial symmetry about the magnetic  $z$ -axis and has a ZFS =  $2|D|$ .

For magnetic complexes of lower symmetry, additional spin operator terms may be needed to accurately specify the resonance spectrum; e.g.,  $(S_x^2 - S_y^2)$  and  $(S_x^4 + S_y^4 + S_z^4)$ , the so-called orthorhombic and cubic terms [26]. The form of the required spin operator terms can sometimes be determined from crystal field theory through the use of equivalent operators, as discussed in [24]. However, the crystal field approach usually assumes ionic bonding and neglects covalency effects. The fact that the coefficients of  $H_s$ , and quite often the form of  $H_s$ , must be determined experimentally (by fitting to EPR data) is quite likely a result of this assumption.

Given an  $H_s$ , one can solve for the spin energy levels and eigenstates by solving:

$$H_s |\psi_i\rangle = E_i |\psi_i\rangle \quad i = 1, 2, \dots, 2S+1 \quad (3)$$

where  $|\psi_i\rangle$  is usually written as a linear combination of pure-spin states,

$$|\psi_i\rangle = a_i |S\rangle + b_i |S-1\rangle + \dots + r_i |-S\rangle \quad (4)$$

and where  $E_i$  is the energy of the  $i$ th level, and  $S$  is the spin of the ion. The labeling of the pure-spin states is identical to the labeling of states for a large applied field. Equation (3) is most easily solved by expressing it in matrix form and using the usual matrix methods to solve for the eigenvalues and eigenvectors of  $H_s$ . Note that  $H_s$  is Hermitian.

Knowing the eigenstates, one may then calculate the rate of stimulated transitions due to an RF magnetic field  $\bar{H}_1$ . Applying Fermi's golden rule, the probability of a transition between states  $i$  and  $j$  is [9]:

$$W_{ij} = \frac{1}{4} \gamma^2 g(f) |\langle \psi_i | g\beta \bar{S} \cdot \bar{H}_1 | \psi_j \rangle|^2 \quad (5)$$

where  $\gamma = g\beta\mu_0/\hbar$ , and  $g(f)$  is the line shape (as a function of frequency) for the transition. The term sandwiched in the matrix element is the magnetic dipole interaction energy. Since non-spin operators may be removed from the matrix element in Eq. (5), it is convenient to define the vector quantity

$$\bar{\sigma}_{ij} = \langle \psi_i | \bar{S} | \psi_j \rangle \quad (6)$$

The vector components are defined by the relation:

$$\bar{\sigma}_{ij} = \frac{1}{2} (\alpha_{ij} \hat{x} + \beta_{ij} \hat{y} + \gamma_{ij} \hat{z}) \quad (7)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are in general complex numbers. Noting Eq. (4),  $\alpha$ ,  $\beta$ , and  $\gamma$  are easily evaluated for any number of spin levels; in [24] the results for a 4-level spin system are given.

As a means of comparing the relative strength of transitions, Siegman [9] has defined the quantity

$$\sigma^2 = \frac{\bar{H}_1^* \cdot \bar{\sigma} \bar{\sigma}^* \cdot \bar{H}_1}{|\bar{H}_1|^2} \quad (8)$$

The stimulated transition probability can then be written as:

$$W_{ij} = \frac{1}{4} \gamma^2 g(f) |\bar{H}_1|^2 \sigma_{ij}^2 \quad (9)$$

The absolute maximum value of  $\sigma^2$  is obtained by using RF fields that are polarized such that  $\bar{H}_1$  is parallel to  $\bar{\sigma}$ . This value of  $\sigma^2$  is given by the trace of  $\bar{\sigma} \bar{\sigma}^*$  [9], which has the value:

$$(\sigma^2)_{\max} = \frac{1}{4} (|\alpha|^2 + |\beta|^2 + |\gamma|^2) \quad (10)$$

This expression will be used to compare transition strengths. This formulation does not consider whether or not the prescribed polarization of  $\bar{H}_1$  is achievable in a given microwave circuit.

The gain of the maser is obviously of central importance and involves several important material parameters. The gain in dB of an unbroadened RWM or TWM [9] is

$$G_{dB} = 27.3 \frac{s\ell}{Q_m} \quad (11)$$

where  $s$  is the slowing factor,  $\ell$  is the maser length in free-space wavelengths, and  $Q_m$  is the magnetic  $Q$  of the maser material. The magnetic  $Q$  is defined as

$$Q_m = \frac{\text{energy stored in material}}{\text{energy emitted per cycle by material}} \quad (12)$$

Assuming  $\frac{hf}{kT} \ll 1$  ( $\frac{hf}{kT} \approx 1/3$  for  $f = 32$  GHz,  $T = 4.2$  K), the reciprocal of  $Q_m$  may be expressed as [9]

$$\frac{1}{Q_m} \approx \frac{\gamma^2 \hbar}{\pi \mu_0} \cdot \frac{hf}{kT} \cdot \frac{I\sigma^2 \eta}{\Delta f_L} \cdot \frac{N}{\text{no. of levels}} \quad (13)$$

where  $I$  is the inversion ratio,  $\eta$  is the filling factor, and  $N$  is the spin density. The filling factor accounts for the fraction of RF field in the material and the degree to which the field is optimally polarized; its value varies between 0 and 1. The spin density is determined by the concentration of paramagnetic ions; for 0.05 percent Cr concentration in ruby,  $N = 2.35 \times 10^{19}$  spins/cm<sup>3</sup>. From Eqs. (11) and (13), we may express  $G_{dB}$  in terms of material parameters as:

$$G_{dB} \propto \frac{I\sigma^2 N}{\Delta f_L \cdot \text{no. of levels}} \quad (14)$$

The inversion ratio is defined as

$$I = \frac{\Delta n_{ij}}{\Delta N_{ji}} \quad (15)$$

where  $\Delta N_{ji} = N_j - N_i$  is the thermal-equilibrium population density-difference, and  $\Delta n_{ij}$  is the population-density difference under pumped conditions. To determine  $I$  for the signal transition of a multi-level spin system, one must solve a set of rate equations that accounts for both stimulated transitions and spin relaxation [9]. These rate equations may be simplified by assuming steady-state conditions and saturated pump levels, and by neglecting the influence of the incoming signal. Since the relaxation rates are not known (this issue will be addressed in the aforementioned future report), the rate equations cannot be solved for the actual inversion ratio. Instead, assumptions are made about the relaxation rates and the corresponding  $I$  is determined. In one case, all relaxation rates are assumed to be equal and the inversion ratio is defined as  $I_{equal}$ . An upper limit can be put on  $I$  by assuming an optimum set of relaxation rates exist [9]. This is defined as  $I_{opt}$ . Note that the actual inversion ratio may be less than both  $I_{opt}$  and  $I_{equal}$ , but for pumping schemes employing two pumps, the actual inversion ratio often lies between  $I_{opt}$  and  $I_{equal}$ . Expressions for  $I_{opt}$  and  $I_{equal}$  are easily derived from the rate equations but will not be given here.

A maser material "figure-of-merit," indicating the gain-bandwidth potential of the material, was proposed [27] to be  $\Delta f_L/Q_m$ . From Eq. (13), and considering only material parameters, we find that

$$\frac{\Delta f_L}{Q_m} \propto \frac{I\sigma^2 N}{\text{no. of levels}} \quad (16)$$

Hence, the figure-of-merit optimizes the product  $G_{dB} \cdot \Delta f_L$ . For the case of a linear stagger-tuned maser with bandwidth  $\Delta f \gg \Delta f_L$ , one can show that the quantity on the right-hand side of Eq. (16) optimizes the product  $G_{dB} \cdot \Delta f$ .

The computer analysis was performed on the JPL UNIVAC (F-system) with a modified version of an existing Fortran code [25] originally written for the analysis of ruby. The JPL Fortran subprogram HERMQR<sup>1</sup> was used to compute the eigenvalues and eigenvectors of  $H_s$ . The existing code was modified to include the spin Hamiltonians of the other materials. Other small modifications were also made.

The inputs to the program are as follows:

- (1) material
- (2) range of  $\theta$  and  $\theta$ -increment
- (3) a single value of  $\phi$
- (4) range of  $B$  and  $B$ -increment
- (5) signal frequency window  $f_{LO}, f_{HI}$
- (6) minimum allowed value for max ( $\alpha, \beta, \gamma$ ) for signal transition,  $\sigma_{min}$

The code is run for a given material at a given  $\phi$ . Typical values are  $\theta = 0$  to 90 deg,  $\Delta\theta = 10$  deg,  $0$  deg  $\leq \phi \leq 90$  deg, and  $B = 0$  to 15 kG,  $\Delta B = 0.5$  kG. For a 32-GHz signal frequency, the window was usually  $f_{LO} = 31$  GHz and  $f_{HI} = 33$  GHz. For transitions falling within this range,  $\sigma_{min} = 1.0$  was chosen. The signal frequency window and  $\sigma_{min}$  are used to pre-select operating points, thus decreasing computer output.

The program outputs are the following:

- (1) energy levels and eigenstates
- (2) transition probabilities (both  $\alpha, \beta, \gamma$  and  $\sigma^2$ )
- (3) local values for  $\frac{\Delta f_s}{\Delta B}$  and  $\frac{\Delta f_p}{\Delta f_s}$
- (4)  $I_{opt}, I_{equal}$ , and figure-of-merit

Because of the large number of possible pumping schemes (especially for the 6-level systems), the following guidelines were employed in choosing schemes:

- (1) signal transition is between adjacent levels
- (2) use two pumps, when possible
- (3) pumps can skip one level at most

These guidelines limit the pumping schemes to the usual ones employed. Many other schemes are possible [9].

<sup>1</sup>JPL Fortran V Subprogram Directory, Fifth Edition, JPL Publication D-829 (internal document), Jet Propulsion Laboratory, Pasadena, California, July 1982.

## IV. Results and Discussion

Table 1 compares several of the more promising operating points of each of the materials analyzed, starting with ruby. The materials are arranged in order of increasing ZFS; for materials with  $S = 5/2$ , the ZFS of the lower degenerate states is used. Across the top of the table is the material name and operating point number. The first row of the table shows the paramagnetic ion used. The second row gives the ZFS. Note that all the materials have a ZFS larger than ruby. The third row indicates the number of magnetically non-equivalent ionic sites in the lattice; a "1" means that all sites are equivalent. The fourth row gives the orientation of  $B$  in terms of the polar and azimuthal angles,  $\theta$  and  $\phi$ , measured with respect to the axes of the magnetic complex. If a value for  $\phi$  is not given, then the Hamiltonian is axially symmetric. For materials with non-equivalent sites,  $\theta$  and  $\phi$  are restricted to values for which the sites are equivalent. The fifth row of the table gives the magnitude of  $B$ . The fields do not exceed 14 kG for the operating points shown.

Rows 6, 7, and 8 list the signal and pump frequencies with the corresponding transition levels shown in parentheses. The signal frequency is always 32.0 GHz. The pump frequencies vary roughly between 50 and 90 GHz. Larger pump frequencies will in general yield larger values of  $I_{opt}$  and  $I_{equal}$ . On the other hand, copper and dielectric losses increase at higher frequencies, with the result that heating of the maser structure may restrict the use of high pump power levels at high frequencies for some materials. Note also that pump frequencies within the same waveguide band simplify engineering issues.

Row 9 gives the value of  $\Delta f_s/\Delta B$  evaluated near the operating point. For a maser tunable over a wide range,  $\Delta f_s/\Delta B$  should be of the same sign and of similar magnitude for the maser material and the isolator material. Rows 10 and 11 give values of  $\Delta f_p/\Delta f_s$  (actually,  $\Delta f_p/\Delta B \cdot \Delta B/\Delta f_s$ ) for both pumps. This parameter is indicative of the pump bandwidth required for a given signal bandwidth, so it is preferable for  $|\Delta f_p/\Delta f_s|$  to be as small as possible. For most of the operating points  $\Delta f_p/\Delta f_s \approx 2$ , but several have values  $< 1$ . Note that  $\Delta f/\Delta B$  is evaluated as a simple two-point difference, with the second point arbitrarily located 200 G from the operating point. For strongly curved energy levels, these values may not be accurate across the desired band.

Rows 12, 13, and 14 give  $\sigma^2$  for the signal and pump transitions for optimum elliptically polarized fields according to Eq. (10). Recall from Eqs. (14) and (16) that  $G_{dB}$  and the figure-of-merit are proportional to  $\sigma_s^2$ , so as large a value of  $\sigma_s^2$  as possible is desired. In general,  $\sigma_s^2$  is a factor of 2- to 3-times larger for the 6-level spin systems. Similarly, a large value of  $\sigma_p^2$  is preferred, since the pump power required for saturation

is inversely proportional to  $\sigma_p^2$ . According to [29], the pump power required for saturation will satisfy

$$P_{pump} \propto \frac{f_p \cdot \Delta f_p}{\sigma_p^2 \tau_p} \quad (17)$$

where  $\tau_p$  is the effective pump relaxation time;  $\tau_p$  is not identical to the measured pump relaxation time. The values of  $\sigma_p^2$  in Table 1 span nearly two orders of magnitude.

Rows 15 and 16 show the inversion ratios for equal and optimum relaxation times. The values of  $I_{equal}$  and  $I_{opt}$  are similar for the various operating points, except when only one pump is employed.

Finally, row 17 gives the material's figure-of-merit, computed in units of MHz, as

$$\frac{\Delta f_L}{Q_m} = \frac{5.6 I_{opt} \cdot \sigma_s^2}{\text{no. of levels}} \quad (18)$$

This follows from Eq. (13) evaluated at  $f = 32$  GHz,  $T = 4.2$  K,  $\eta = 0.5$ , and  $N = 2.35 \times 10^{19}$  spins/cm<sup>3</sup>. Since the true inversion ratio for a given operating point may be as much as a factor of 3 or more smaller than  $I_{opt}$ , a detailed comparison of figure-of-merits could be misleading.

Table 1 is by no means complete in the sense that one may confidently select the best maser material from it. Two very important parameters are missing: the actual inversion ratio and the pump power,  $P_{pump}$ , required to maintain that inversion ratio. At present, both of these parameters must be measured.

Since both  $I$  and  $P_{pump}$  depend critically on relaxation times, a table of relaxation times, located in the Appendix and labeled Table A, was compiled from data found in the literature. Ionic concentration, frequency, orientation, and transition information is included. Because these parameters do not coincide with pump operating-points of interest to us, and because of the dependence of relaxation times on measurement technique and crystal growth procedures [30], the data in Table A could easily be an order of magnitude or more different from what would be measured for the materials in Table 1. Hence, the relaxation times in Table A are not used in any calculations in this work, even though they are the best values available to us at the present time.

Before discussing the many materials in Table 1, consider the operating point in which ruby is presently being used at 32 GHz (first column of table, Ruby No. 1). The ruby is oriented at the double-pump angle ( $\theta = 54.7$  deg) and pumped

in the push-pull mode, so the pump frequencies are equal. Scanning down the column, two potential problems can be seen with this operating point. First, the pump bandwidths are nearly twice the signal bandwidths, so if 500 MHz of signal bandwidth is desired at 32 GHz, 1-GHz bandwidth must be pumped at 66 GHz. To pump such a large bandwidth, the pumps must be swept across the band, effectively reducing the pump power at a given frequency. How detrimental this is depends on the relaxation times of the pump transitions.

The second problem with ruby at this operating point is the weak pump transitions:  $\sigma_{p1}^2 = 0.05$  and  $\sigma_{p2}^2 = 0.04$  compared to  $\sigma_s^2 = 1.92$ . For this reason, high levels of pump power are used in the 32-GHz RWM, although the pumped levels are still not saturated. Note that a small  $\sigma_p^2$  does not preclude good maser performance, as demonstrated by the 18- to 26-GHz maser of Moore and Clauss [2], [31] for which  $\sigma_{p1}^2 = 0.07$  and  $\sigma_{p2}^2 = 0.11$ .

The most significant problem with ruby, the low inversion ratio, is not indicated by the table. Measured values of  $I$  for the case of saturated pump transitions have been approximately 1.1 ([3], and J. Shell, private communication). (The similarity to  $I_{equal} = 1.1$  does not necessarily mean that the relaxation times are equal.) In the 18- to 26-GHz range, measured values of  $I$  have been in the range of 1.6 to 1.8 [2], [3], [31].

Finally, from Table A it can be seen that ruby has long relaxation times compared to the other materials. Hence, even though  $\sigma_p^2$  is small, the denominator of Eq. (17) remains large enough for ruby to require large but manageable pump power.

Consider several other operating points in Table 1. Since ruby has worked so well in the past, ruby at another orientation is an obvious candidate for a maser material. The second column of the table, Ruby No. 2, shows ruby at  $\theta = 90$  deg and with a push-push pumping scheme. Even though  $\sigma_s^2$  and  $\sigma_{p1}^2$  are weaker and the values for  $I_{equal}$  and  $I_{opt}$  are less than for Ruby No. 1, if the actual inversion ratio is  $>1.5$ , Ruby No. 2 could yield a higher gain-bandwidth product. Some investigators [4] claim Ruby No. 2 to be superior to Ruby No. 1 at millimeter wavelengths because of a higher inversion ratio and less critical orientation (less spreading of pump power due to c-axis wander).

The sapphire host has many desirable properties, so Fe-doped sapphire is a logical choice. For Sapphire No. 1,  $\sigma_p^2$  is 2- to 5-times stronger than that of Ruby No. 1 and  $\sigma_s^2$  is 2- to 3-times that of Ruby No. 1. However, according to Table A, the pump relaxation times may be an order of magnitude shorter, implying that Sapphire No. 1 could require several times the pump power of Ruby No. 1. Other investigators

[28] suggest that the relaxation times of Fe-doped sapphire are similar to those of ruby. If this is true, then Sapphire No. 1 could require several times less pump power than Ruby No. 1. Measurements of the relaxation times and pump power required must be made to determine which scenario is correct.

Emerald has some similarity to ruby, having the same spin Hamiltonian and potentially long relaxation times. If the inversion ratio for Emerald No. 1 is  $\geq 2$ , then this operating point would be very attractive. A problem with emerald is the difficulty of its growth, which may not allow the high degree of crystal perfection necessary.

Zinc tungstate has a complicated  $H_s$ , large ZFS values, and may have short relaxation times, making it quite different from ruby. Cr-doped zinc tungstate has several promising operating points. In particular,  $ZnWO_4$  No. 1 is attractive, assuming  $I \approx I_{opt}$ . Fe-doped zinc tungstate exhibits a large number of excellent operating points. For  $ZnWO_4$  No. 3,  $\sigma_s^2$  is 2- to 3-times greater than that of Ruby No. 1 and  $\sigma_p^2$  is 100 times that of Ruby No. 1. This large value of  $\sigma_p^2$  raises the question of whether it is preferable to have large  $\sigma_p^2$  and small  $\tau_p$  ( $ZnWO_4$  No. 3) or small  $\sigma_p^2$  and large  $\tau_p$  (Ruby No. 1). Assuming the product  $\sigma_p^2 \cdot \tau_p$  is constant, the pump power requirements will be similar, but in the former case more energy would be transferred to the lattice. This could raise the temperature of the maser material, thereby decreasing the gain; however, this possibility has not been considered in detail. Harmonic cross relaxation may be a problem for several of the better operating points for  $ZnWO_4:Fe$ . One similarity zinc tungstate has with ruby is that it can be grown by the Czochralski method.

The rutiles appear promising, but the large, anisotropic, temperature-dependent dielectric constant of rutile makes it unattractive from an engineering standpoint.

One can easily see from Table 1 that many of the other materials analyzed may make excellent maser materials, but the lack of information on inversion ratios, pump power requirements, relaxation times, etc., makes them difficult to evaluate.

Another possibility, not addressed in Table 1, is to use standard ruby doped with a fast-relaxing impurity. This additional impurity may be added in the melt or created in the finished ruby by exposure to X-rays (so-called orange-ruby [9]). A properly chosen impurity can shorten certain relaxation times, which, by making the times more optimal, can increase the inversion ratio. However, the impurity would not alter the ZFS, so the pump transitions would still be weak.

We hope to eventually make measurements of inversion ratios, pump power requirements, and relaxation times at

32 GHz and around 60 GHz on several of the materials in Table 1.

Other materials we would like to analyze but for which we do not have the spin Hamiltonians are spinel:Fe and chrysoberyl:Cr, Fe.

## V. Conclusions and Future Work

Any of the materials analyzed in this work may yield better maser performance than does ruby at 32 GHz at the double-pump angle. However, several key parameters related to pump power requirements may eliminate some or all of these materials. Based on results from the analysis of the spin Hamiltonians and on scanty (and unreliable) relaxation time data, several materials show particular promise (e.g., Fe-doped zinc tungstate).

To complete the materials evaluation, it will be necessary to measure the inversion ratio and pump power required for saturation for each operating-point of interest. Barring cross-relaxation and other concentration-dependent effects, knowledge of the relaxation-times would be sufficient to calculate both  $I$  and  $P_{pump}$ . However, the subtlety of measuring relaxation-times will most likely require that  $I$  and  $P_{pump}$  be measured.

Better understanding of the low inversion ratio of ruby is needed. By accounting for the spin-phonon interaction, one can calculate the relaxation rates of the transitions for low spin concentrations [29]. With these relaxation rates, the inversion ratios and pump power requirements can be calculated for each operating-point of interest and for various physical temperatures.

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## References

- [1] S. Petty, "Introduction to Microwave Devices, Part VIII," in *Low Temperature Electronics*, edited by R. Kirschman, New York: IEEE Press, 1986.
- [2] C. Moore and R. Clauss, "A Reflected-Wave Ruby Maser with K-Band Tuning Range and Large Instantaneous Bandwidth," *IEEE Trans. Microwave Theory Tech.*, vol. MTT-27, pp. 249–256, March 1979.
- [3] C. Moore and D. Neff, "Experimental Evaluation of Ruby at 43 GHz," *IEEE Trans. Microwave Theory Tech.*, vol. MTT-30, pp. 2013–2015, Nov. 1982.
- [4] A. Blinov and S. Peskovatskii, "Inversion Characteristics of Ruby at the Center of the Millimeter Band," *Radiofizika*, vol. 30, pp. 784–787, 1987.
- [5] J. Shell and D. Neff, "A 32 GHz Reflected-Wave Maser Amplifier with Wide Instantaneous Bandwidth," in *Conference Digest, IEEE MTT-S International Microwave Symposium*, New York, May 1988.
- [6] J. Orton, D. Paxman, and J. Walling, *The Solid State Maser*, Oxford: Pergamon Press Ltd., Chapter 2, Maser Materials, 1970.
- [7] W. Low, "Paramagnetic Substances Suitable for Maser Operation in the Millimeter Range," in *Conference Proceedings, Symposium on Millimeter Waves*, Polytechnic Institute of Brooklyn, March 31, April 1–2, 1959.
- [8] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, New York: Dover, 1986.
- [9] A. Siegman, *Microwave Solid-State Masers*, New York: McGraw-Hill, 1964.
- [10] Schiff, *Quantum Mechanics*, 3rd ed., New York: McGraw-Hill, 1968.
- [11] E. Schulz-Du Bois, "Paramagnetic Spectra of Substituted Sapphires—Part 1: Ruby," *Bell Syst. Tech J.*, vol. 38, pp. 271–290, 1959.
- [12] J. Geusic, M. Peter, and E. Schulz-Du Bois, "Paramagnetic Resonance Spectrum of CR<sup>3+</sup> in Emerald," *Bell Syst. Tech. J.*, vol. 38, pp. 291–296, 1959.
- [13] R. Stahl-Brada and W. Low, "Paramagnetic Resonance Spectra of Chromium and Manganese in the Spinel Structure," *Phys. Rev.*, vol. 116, pp. 561–564, 1959.
- [14] J. Carson and R. White, "Zero-Field Splitting of the Cr<sup>3+</sup> Ground State of YGa and YAl Garnet," *J. Appl. Phys.*, vol. 32, p. 1787, 1961.
- [15] H. Gerritsen, S. Harrison, and H. Lewis, "Chromium-Doped Titania as a Maser Material," *J. Appl. Phys.*, vol. 31, pp. 1566–1571, 1960.
- [16] S. Kurtz and W. Nilsen, "Paramagnetic Resonance Spectra of Cr<sup>3+</sup> in ZnWO<sub>4</sub>," *Phys. Rev.*, vol. 128, pp. 1586–1588, 1962.
- [17] V. Vinokurov, et al., "Paramagnetic Resonance of Trivalent Chromium in Andalusite," *Sov. Phys.—Solid State*, vol. 4, pp. 470–472, 1962.
- [18] J. Carson, D. Devon, and R. Hoskins, "Paramagnetic Resonance of Cr<sup>3+</sup> in Yttrium Oxide," *Phys. Rev.*, vol. 122, pp. 1141–1143, 1961.
- [19] D. Carter and A. Okaya, "Electron Paramagnetic Resonance of Fe<sup>3+</sup> in TiO<sub>2</sub> (Rutile)," *Phys. Rev.*, vol. 118, pp. 1485–1490, 1960.
- [20] W. Nilsen and S. Kurtz, "Paramagnetic Resonance Spectra of Fe<sup>3+</sup> in ZnWO<sub>4</sub>," *Phys. Rev.*, vol. 136, pp. A262–A266, 1964.

- [21] F. Holuj, J. Thyen, and N. Hedgecock, "ESR Spectra of  $\text{Fe}^{3+}$  in Single Crystals of Andalusite," *Can. J. Phys.*, vol. 44, pp. 509–523, 1966.
- [22] G. Bogle and H. Symmons, "Paramagnetic Resonance of  $\text{Fe}^{3+}$  in Sapphire at Low Temperatures," *Proc. Phys. Soc. (London)*, vol. 73, pp. 531–532, 1959.
- [23] B. Bleaney and W. Stevens, "Paramagnetic Resonance," *Reports on Prog. Phys.*, vol. 16, pp. 108–159, 1953.
- [24] R. Berwin, "Paramagnetic Energy Levels of the Ground State of  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$  (Ruby)," *Technical Memorandum, 33-440*, Jet Propulsion Laboratory, Pasadena, California, January 1970.
- [25] R. Berwin, "Energy Levels and Transition Matrix Elements of Paramagnetic Crystals for Maser Applications," *Technical Memorandum, 33-446*, Jet Propulsion Laboratory, Pasadena, California, March 1970.
- [26] J. Orton, "Paramagnetic Resonance Data," *Rep. Prog. Phys.*, vol. 22, pp. 204–240, 1959.
- [27] R. Berwin, R. Clauss, and E. Wiebe, "Low-Noise Receivers: Microwave Maser Development," *JPL Space Programs Summary, 37-56*, vol. II, Jet Propulsion Laboratory, Pasadena, California, March 1969.
- [28] K. Standley and R. Vaughan, "Effect of Crystal-Growth Method on Electron Spin Relaxation in Ruby," *Phys. Rev.*, vol. 139, pp. A1275–A1280, 1965.
- [29] V. Shakhparyan and R. Martirosyan, "Inversion Ratio Studies of Ruby in High-Intensity Magnetic Field," *Phys. Stat. Sol. (a)*, vol. 25, pp. 681–690, 1974.
- [30] K. Standley and R. Vaughan, *Electron Spin Resonance Phenomena in Solids*, London: Adam Hilger LTD, 1969.
- [31] C. Moore, "A K-Band Ruby Maser with 500-MHz Bandwidth," *IEEE Trans. Microwave Theory Tech.*, vol. MTT-28, pp. 149–151, Feb. 1980.
- [32] J. Pace, D. Sampson, and J. Thorp, "Spin-Lattice Relaxation Times in Ruby at 34.6 Gc/s," *Proc. Phys. Soc.*, vol. 76, p. 697, 1960.
- [33] D. Mason and J. Thorp, "Influence of Crystalline Imperfections on Spin-Lattice Relaxation in Ruby," *Phys. Rev.*, vol. 157, p. 191, 1967.
- [34] J. Pace, D. Sampson, and J. Thorp, "Spin-Lattice Relaxation Times in Sapphire and Chromium-doped Rutile at 34.6 Gc/s," *Proc. Phys. Soc.*, vol. 77, p. 257, 1961.
- [35] P. Squire and J. Orton, "Relaxation of the  $\text{Cr}^{3+}$  Ion in Emerald," *Proc. Phys. Soc.*, vol. 88, pp. 649–657, 1966.
- [36] J. Orton, A. Fruin, and J. Walling, "Spin-Lattice Relaxation of  $\text{Cr}^{3+}$  in Single Crystals of Zinc Tungstate," *Proc. Phys. Soc.*, vol. 87, pp. 703–716, 1966.
- [37] M. Madan, "Spin-Lattice Relaxation Time of  $\text{Fe}^{3+}$  Ions," *Can. J. Phys.*, vol. 42, pp. 583–594, 1964.

**Table 1. Promising 32-GHz operating points for ruby and other materials. The materials are arranged in order of increasing ZFS.**

Operating Point	Material					
	Ruby No. 1	Ruby No. 2	Ruby No. 3	Sapphire No. 1	Sapphire No. 2	YAG No. 1
Ion	Cr	Cr	Cr	Fe	Fe	Cr
ZFS, GHz	11.4	11.4	11.4	12.1, 19.1	12.1, 19.1	15.7
No. of ionic sites	1	1	1	2	2	1
$\theta, \phi$ , deg	54.74	90	90	90, 45	60, 30	54.74
B, kG	11.81	13.50	11.20	9.50	12.44	13.27
$f_s$ , GHz	32.0 (32)	32.0 (21)	32.0 (32)	32.0 (32)	32.0 (54)	32.0 (32)
$f_{p1}$	66.2 (13)	70.3 (13)	57.6 (13)	68.6 (13)	77.3 (13)	76.2 (13)
$f_{p2}$	66.2 (24)	43.3 (34)	68.9 (24)	59.9 (24)	66.1 (35)	76.2 (24)
$\Delta f_s/\Delta B$ , MHz/G	2.9	2.8	2.7	2.8	3.0	2.9
$\Delta f_{p1}/\Delta f_s$	1.9	2.0	2.0	2.0	1.8	1.8
$\Delta f_{p2}/\Delta f_s$	1.9	1.0	2.0	2.0	2.0	1.8
$\sigma_s^2$	1.92	1.51	1.97	6.87	5.64	1.62
$\sigma_{p1}^2$	0.05	0.02	0.03	0.08	0.09	0.13
$\sigma_{p2}^2$	0.04	1.51	0.02	0.17	0.28	0.31
$I_{opt}$	3.1	2.2	2.8	3.0	4.8	3.7
$I_{equal}$	1.1	0.7	0.9	1.0	2.0	1.4
$\Delta f_L/Q_m$ , MHz	8.3	4.7	7.7	19.2	25.3	8.4

Operating Point	Material					
	YAG No. 2	YGG No. 1	YGG No. 2	Spinel No. 1	Andalusite No. 1	Andalusite No. 2
Ion	Cr	Cr	Cr	Cr	Cr	Cr
ZFS, GHz	15.7	20.9	20.9	29.7	32.0	32.0
No. of ionic sites	1	1	1	4	2	2
$\theta, \phi$ , deg	70	54.74	70	54.74	55.0	70.0
B, kG	13.40	13.96	13.35	13.15	12.94	13.00
$f_s$ , GHz	32.0 (43)	32.0 (32)	32.0 (43)	32.0 (32)	32.0 (32)	32.0 (43)
$f_{p1}$	49.6 (12)	81.8 (13)	53.3 (12)	75.3 (13)	74.2 (13)	47.0 (12)
$f_{p2}$	69.7 (24)	81.8 (24)	70.7 (24)	75.3 (24)	75.8 (24)	69.4 (24)
$\Delta f_s/\Delta B$ , MHz/G	2.4	2.7	2.2	2.9	2.8	2.4
$\Delta f_{p1}/\Delta f_s$	1.2	1.9	1.3	1.8	1.9	1.1
$\Delta f_{p2}/\Delta f_s$	2.1	1.9	2.1	1.8	1.9	2.1
$\sigma_s^2$	1.25	1.50	1.01	1.66	1.63	1.27
$\sigma_{p1}^2$	1.52	0.16	1.54	0.28	0.15	1.53
$\sigma_{p2}^2$	0.31	0.47	0.55	0.13	0.31	0.31
$I_{opt}$	3.6	4.0	3.9	3.6	3.6	3.5
$I_{equal}$	1.5	1.6	1.6	1.4	1.4	1.4
$\Delta f_L/Q_m$ , MHz	6.3	8.4	5.5	8.4	8.2	6.2

**Table 1 (contd)**

Operating Point	Material					
	Rutile No. 1	Rutile No. 2	Rutile No. 3	Rutile No. 4	ZnWO <sub>4</sub> No. 1	ZnWO <sub>4</sub> No. 2
Ion	Cr	Cr	Fe	Fe	Cr	Cr
ZFS, GHz	43.3	43.3	43.3, 81.3	43.3, 81.3	51.6	51.6
No. of ionic sites	2	2	2	2	1	1
$\theta, \phi, \text{deg}$	45, 0	54.74, 45	52.55, 40	71.12, 70	40, 90	50, 90
B, kG	12.78	14.06	9.35	11.71	9.78	13.10
$f_s$ , GHz	32.0 (43)	32.0 (32)	32.0 (32)	32.0 (43)	32.0 (21)	32.0 (32)
$f_{p1}$	56.0 (12)	82.6 (13)	78.9 (13)	71.8 (12)	54.1 (13)	75.1 (13)
$f_{p2}$	65.4 (24)	82.6 (24)	73.3 (24)	81.4 (24)	54.9 (34)	88.4 (24)
$\Delta f_s/\Delta B$ , MHz/G	2.0	2.6	2.8	3.7	2.3	1.9
$\Delta f_{p1}/\Delta f_s$	1.5	1.9	2.1	0.9	1.1	2.2
$\Delta f_{p2}/\Delta f_s$	2.2	1.9	2.1	2.1	1.8	2.6
$\sigma_s^2$	1.57	1.37	3.80	3.57	1.68	1.37
$\sigma_{p1}^2$	1.18	0.48	0.67	3.31	0.53	0.31
$\sigma_{p2}^2$	0.37	0.30	1.55	1.01	0.57	0.61
$I_{opt}$	3.7	4.1	3.7	5.7	2.1	3.8
$I_{equal}$	1.4	1.6	1.4	2.6	0.5	1.5
$\Delta f_L/Q_m$ , MHz	8.1	7.9	13.1	19.0	4.9	7.3

  

Operating Point	Material					
	Emerald No. 1	Emerald No. 2	ZnWO <sub>4</sub> No. 3	ZnWO <sub>4</sub> No. 4	Y <sub>2</sub> O <sub>3</sub> No. 1	Andalusite No. 3
Ion	Cr	Cr	Fe	Fe	Cr	Fe
ZFS, GHz	53.5	53.5	61.0, 76.9	61.0, 76.9	72.7	112.6, 225.2
No. of ionic sites	1	1	1	1	4	2
$\theta, \phi, \text{deg}$	40, 0	54.74	90, 45	90, 45	40	30, 0
B, kG	7.95	14.04	8.59	5.28	9.14	6.63
$f_s$ , GHz	32.0 (43)	32.0 (32)	32.0 (54)	32.0 (54)	32.0 (21)	32.0 (21)
$f_{p1}$	48.4 (12)	86.1 (13)	66.0 (13)	67.9 (13)	69.1 (13)	107.3 (13)
$f_{p2}$	50.8 (24)	86.1 (24)	67.4 (35)	57.6 (35)	88.3 (24)	—
$\Delta f_s/\Delta B$ , MHz/G	3.5	2.2	2.1	-2.7	-3.32	4.78
$\Delta f_{p1}/\Delta f_s$	1.5	2.2	-0.1	0.4	-0.16	-0.07
$\Delta f_{p2}/\Delta f_s$	0.3	2.2	2.1	-0.5	-0.72	—
$\sigma_s^2$	1.54	1.38	5.52	3.24	0.76	3.55
$\sigma_{p1}^2$	0.13	0.66	3.01	3.17	0.73	2.32
$\sigma_{p2}^2$	0.59	0.19	2.91	3.51	1.31	—
$I_{opt}$	2.6	4.3	4.3	3.8	3.6	2.0
$I_{equal}$	0.8	1.7	1.8	1.5	1.4	0.5
$\Delta f_L/Q_m$ , MHz	5.6	8.3	22.2	11.5	3.8	6.6

## Appendix

### Table of Relaxation Times

This Appendix contains a table of relaxation times ( $T_1$ ) for various materials at 4.2 K. The paramagnetic ion concentration, transition frequency, transition, and orientation are also shown. In addition, the literature references are included. Note that the table does not mention either the crystal growth

process or the relaxation time measurement technique, both of which may significantly alter the reported relaxations times. Hence, these relaxation times could easily be an order of magnitude or more different from what one might measure, and should not be used in calculations unless verified.

**Table A-1. Measured relaxation times,  $T_1$ , for various materials at physical temperature  $T = 4.2^\circ\text{K}$**

Material	Ionic concentration, atomic percent	Frequency, GHz	Orientation, deg ( $\theta, \phi$ )	Transition	$T_1$ , msec	Reference
Ruby	0.03	34.6	90	3-4	21	[32]
				2-3	16	
				1-2	22	
				2-4	54	
				1-3	56	
	0.013 0.052	35	90	2-3 2-3	15.5 17.5	[33]
Sapphire: Fe	0.03	34.6	90, 0	4-5	1.8	[34]
				3-4	1.6	
				2-3	1.5	
				1-2	2.0	
	$4.9 \times 10^{19}$ ions/cm <sup>3</sup>	9.3	0 90	3-4 1-2 3-4	9 8 11	[35]
$\text{ZnWO}_4$ : Cr	0.005-0.3	9.2	90, 90	1-2	$\approx 1.5$	[36]
	0.018-0.72			1-2	$\approx 0.5$	
	0.08	X-band	?	5-6 1-2	$\sim 0.3$ $\sim 1$	a
Rutile: Cr	0.07	34.6	90, 0 <sup>b</sup>	1-2 3-4	4.5 2.5	[34]
				2-3 2-4	2.5 2.1	
Rutile: Fe	0.01-0.02	9.4	0, 0	1-2 3-4	$\approx 2$ $\approx 2$	[37]

<sup>a</sup>J. Orton, private communication with K. Standley and R. Vaughan.

<sup>b</sup>For this orientation the ionic sites are inequivalent.